



## Synthesis and Crystal Structure of Trinuclear Copper(I/II) Complex $[\text{Cu}(\text{pa})_2][\text{Cu}(\text{pht})_2]_2$

XI-LAN HU<sup>1,2</sup>, FU-JUN YIN<sup>1,2,\*</sup>, PENG-FEI SHI<sup>1,2</sup>, DA-QI WANG<sup>3</sup> and XU-RUI BO<sup>1</sup>

<sup>1</sup>School of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

<sup>2</sup>Jiangsu Deveronmentresearch Insitute of Marine Resources, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

<sup>3</sup>College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P.R. China

\*Corresponding author: E-mail: yinfujun2008@126.com

Received: 11 November 2014;

Accepted: 30 December 2014;

Published online: 26 May 2015;

AJC-17264

A novel trinuclear copper(I/II) complex  $[\text{Cu}(\text{pa})_2][\text{Cu}(\text{pht})_2]_2$  (pa = 1,3-propylenediamine, Hpht = 5,5-diphenylhydantoin, *i.e.* phenytoin) has been synthesized under hydrothermal condition and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The trinuclear Cu(I/II) complex is triclinic, space group  $P\bar{1}$ , with  $a = 8.6506(12)$ ,  $b = 11.8844(16)$ ,  $c = 15.367(2)$  Å,  $\alpha = 98.5940(10)$ ,  $\beta = 92.2810(10)$ ,  $\gamma = 104.188(2)^\circ$ ,  $Z = 1$ ,  $D_c = 1.478$  g/cm<sup>3</sup>,  $\mu = 1.115$  mm<sup>-1</sup>, the final  $R = 0.0812$  and  $wR = 0.2029$ . The complex consists of an interesting trinuclear copper(I/II) unit. In the crystal structure, each Cu(I) ion is linearly coordinated by  $N_2$  and  $N_4$  from two different 5,5-diphenylhydantoin, respectively and the six coordinated Cu(II) ion adopted a distorted octahedral geometry.

**Keywords:** Copper(I/II), Complex, Phenytoin.

### INTRODUCTION

Phenytoin (5,5-diphenylimidazoline-2,4-dione, Hpht) is a widely used drug in the treatment of epilepsy<sup>1,2</sup>. Phenytoin is also an excellent ligand because it contains two amide and one carbonyl groups which can provide strong [N,O] coordinating potential to metal ions<sup>3-14</sup>. The interests in the complexes of transition metals with phenytoin ligand owed to their fascinating structural diversity. However, to the best of our knowledge, no study on the crystal structure of copper complex with phenytoin and 1,3-propylenediamine has been reported yet. Herein we report the synthesis and characterization of a novel trinuclear copper complex.

### EXPERIMENTAL

All starting materials were of chemical purity. The solvents used in the physical measurements were of analytical purity. Elemental analysis was determined with a Perkin-Elmer 240C instrument. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer.

**Preparation of  $[\text{Cu}(\text{pa})_2][\text{Cu}(\text{pht})_2]_2$ :**  $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  (0.1998 g, 1 mmol) and phenytoin (0.2511 g, 1 mmol) were dissolved in methanol and 2.5 mL 0.4 mol/L 1,3-pa (1 mmol) was added slowly to the above solution. Then the mixture was sealed in a 25 mL stainless steel vessel with Teflon liner and heated to 393 K for 50 h with 80 % compactness. After cooling

to room temperature, block-like blue crystals were obtained in 54.36 %; yield. m.p.: 577 K. Anal; found: C 58.81, H 4.59, N 12.31 %; calculated for  $\text{C}_{66}\text{H}_{64}\text{N}_{12}\text{O}_8\text{Cu}_3$ : C 58.99, H 4.80, N 12.51 %.

**Structure determination:** Suitable crystal of complex was mounted on a glass fiber. The crystal data were collected at 298(2) K on a Bruker SMART/CCD area-detector diffractometer with graphite monochromatic  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 7748 reflections were collected with 5218 unique ones ( $R_{\text{int}} = 0.0485$ ), of which 3304 observed reflections with  $I > 2\sigma(I)$  were used in the succeeding refinements. Intensity data were corrected for  $L_p$  factors and empirical absorption. The structure was solved by direct methods. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares technique on  $F^2$  with anisotropic thermal parameters for all non hydrogen atoms. The hydrogen atoms were added according to the theoretical models. The final full matrix least-squares refinement gave  $R = 0.0812$  and  $wR = 0.2029$  ( $w = 1/[\sigma^2(F_o^2) + (0.1447P)^2 + 0.0000P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ). The maximum and minimum peaks on the final difference fourier map corresponded to + 1.379 and  $-1.091 \text{ e} \times \text{Å}^{-3}$ , respectively. All calculations were performed using the programs contained in the SHELXL-97<sup>15</sup>. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the complex were located from the difference fourier maps and refined isotropically.

## RESULTS AND DISCUSSION

The IR spectrum displays strong broad around 3334 and 3432  $\text{cm}^{-1}$ , which can be ascribed to the N-H stretching vibration of 1,3-pa. The strong peaks appear at 1640 and 1383  $\text{cm}^{-1}$  can be assigned to the symmetric and asymmetric stretching modes of the amide I band and C=O, respectively, with the  $\Delta$  value of 214  $\text{cm}^{-1}$ .

The atomic coordinates and equivalent isotropic displacement parameters for the  $[\text{Cu}(\text{pa})_2][\text{Cu}(\text{pht})_2]$  are listed in Table-1, the selected bond lengths and bond angles in Table-2 and the hydrogen bonds bond and its lengths and bond angles in Tables-3, respectively.

The X-ray diffraction analysis shows that the complex has a trinuclear structure. An asymmetric unit in the crystal

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR COMPLEX

Empirical formula	$\text{C}_{66}\text{H}_{64}\text{N}_{12}\text{O}_8\text{Cu}_3$	$\gamma$ (°)	104.188(2)
Formula weight	1343.91	$V/\text{\AA}^3$	1509.6(4)
Color/habit	Blue/square	$D/(\text{Mg m}^{-3})$	1.478
Size/mm	$0.40 \times 0.38 \times 0.35$	Z	1
$\theta$ Range for data collection	1.34 to 25.01	F(000)	659
Crystal system	Triclinic	$\mu(\text{MoK}\alpha)$ ( $\text{mm}^{-1}$ )	1.115
Space group	Pi	Reflections collections	7748
$a/\text{\AA}$	8.6506(12)	Independent reflections	5218 ( $R_{\text{int}} = 0.0485$ )
$b/\text{\AA}$	11.8844(16)	$R_1, wR_2(I > 2\sigma(I))$	0.0812, 0.2029
$c/\text{\AA}$	15.367(2)	$R_1, wR_2$ (all data)	0.1267 0.2448
$\alpha$ (°)	98.5940(10)	Largest diff. peak and hole ( $\text{\AA}^{-3}$ )	1.379, -1.091
$\beta$ (°)	92.2810(10)	S	1.030

TABLE-2  
SELECTED BOND DISTANCES ( $\text{\AA}$ ) AND ANGLES (°) FOR COMPLEX

Bond length	$\text{\AA}$	Bond length	$\text{\AA}$
Cu(1)-N(4)	1.861(5)	Cu(2)-N(6)#1	1.84(4)
Cu(1)-N(2)	1.863(5)	Cu(2)-N(5)	2.03(3)
Cu(2)-Cu(2)#1	0.717(5)	Cu(2)-N(6)	2.05(4)
Cu(2)-N(5)#1	1.75(2)	Cu(2)-N(6')	2.41(5)
Cu(2)-N(5')#1	2.04(3)	Cu(2)-N(5')	2.51(4)
Cu(2)-N(6')#1	2.05(5)	Cu(2)-O(3)	2.377(5)
Angle	(°)	Angle	(°)
N(4)-Cu(1)-N(2)	177.0(2)	N(6)#1-Cu(2)-O(3)	108.5(11)
Cu(2)#1-Cu(2)-N(5)#1	102.7(16)	N(5)-Cu(2)-O(3)	98.7(9)
Cu(2)#1-Cu(2)-N(6)#1	96.6(14)	N(5')#1-Cu(2)-O(3)	82.1(10)
N(5)#1-Cu(2)-N(6)#1	106.5(15)	N(6')#1-Cu(2)-O(3)	97.8(12)
Cu(2)#1-Cu(2)-N(5)	57.2(13)	N(6)-Cu(2)-O(3)	89.2(10)
N(5)#1-Cu(2)-N(5)	159.9(4)	Cu(2)#1-Cu(2)-N(6')	52.0(13)
N(6)#1-Cu(2)-N(5)	78.2(15)	N(5)#1-Cu(2)-N(6')	88.6(19)
Cu(2)#1-Cu(2)-N(5')#1	123.6(15)	N(6)#1-Cu(2)-N(6')	148.0(12)
N(5)#1-Cu(2)-N(5')#1	21.0(8)	N(5)-Cu(2)-N(6')	78.7(18)
N(6)#1-Cu(2)-N(5')#1	99.1(16)	N(5')#1-Cu(2)-N(6')	103.8(19)
N(5)-Cu(2)-N(5')#1	177.3(12)	N(6')#1-Cu(2)-N(6')	164.0(4)
Cu(2)#1-Cu(2)-N(6')#1	112.1(15)	N(6)-Cu(2)-N(6')	12.5(13)
N(5)#1-Cu(2)-N(6')#1	96.1(19)	O(3)-Cu(2)-N(6')	96.7(10)
N(6)#1-Cu(2)-N(6')#1	16.7(11)	Cu(2)#1-Cu(2)-N(5')	42.6(11)
N(5)-Cu(2)-N(6')#1	92.3(18)	N(5)#1-Cu(2)-N(5')	145.3(9)
N(5')#1-Cu(2)-N(6')#1	85(2)	N(6)#1-Cu(2)-N(5')	84.5(15)
Cu(2)#1-Cu(2)-N(6)	63.1(12)	N(5)-Cu(2)-N(5')	14.7(9)
N(5)#1-Cu(2)-N(6)	79.7(16)	N(5')#1-Cu(2)-N(5')	166.2(4)
N(6)#1-Cu(2)-N(6)	159.7(4)	N(6')#1-Cu(2)-N(5')	100.3(18)
N(5)-Cu(2)-N(6)	89.7(15)	N(6)-Cu(2)-N(5')	80.2(14)
N(5')#1-Cu(2)-N(6)	92.9(16)	O(3)-Cu(2)-N(5')	109.5(7)
N(6')#1-Cu(2)-N(6)	172(2)	N(6')-Cu(2)-N(5')	68.3(16)
$\backslash\text{Cu(2)\#1-Cu(2)-O(3)}$	141.0(9)	—	—

Symmetry transformation: a:  $-x + 2, -y + 3, -z + 1$

TABLE-3  
DISTANCE ( $\text{\AA}$ ) AND ANGLES (°) OF HYDROGEN BONDS FOR THE COMPLEX

D-H...A	Distance (D...A)	Angle (D-H-A)	Symmetry code
N1-H1...O4	2.933	163.06	$-x + 3, -y + 2, -z + 1$
N3-H3...O2	2.879	165.34	$x + 3, -y + 3, -z + 1$
N5-H5A_a...O3	3.147	126.32	$-x + 2, -y + 3, -z + 1$
N5'-H5'1_b...O4	3.414	142.40	$x-1, y, z$
N6-H6B_a...O2	3.149	136.75	$x-1, y, z$

structure of the title compound  $[\text{Cu}(\text{pa})_2][\text{Cu}(\text{pht})_2]_2$  consists of one molecule of *bis*(5,5-diphenylhydantoinato)copper(II) and half molecule of *bis*(1,3-propylenediamine)copper(II) (Fig. 1). In the crystal structure, Cu(2) is in an octahedral *trans*- $\text{CuN}_4\text{O}_2$  coordination environment and lies on a center of symmetry. The phenytoin ligands act as monodentate ligand and the 1,3-propylenediamine ligand acts as bidentate ligand, respectively. The Cu-N bond distances lie in the range of 1.86 (5) to 2.51 (4) Å. Adjacent molecules are linked by intermolecular hydrogen bonds along the crystallographic axis (Fig. 2). This pattern of hydrogen-bonding interactions is also found in the above-mentioned related complexes.

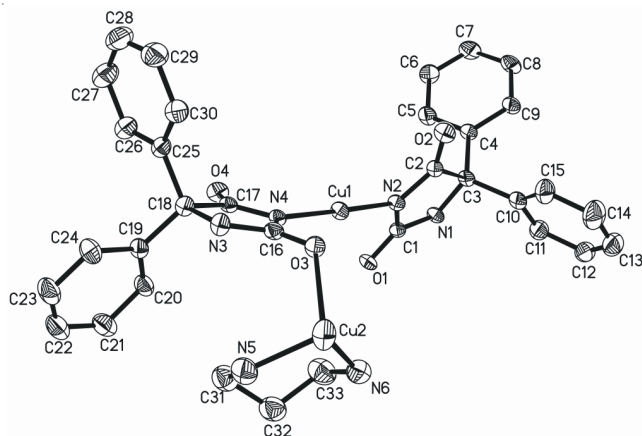


Fig. 1. Crystal structure of the asymmetric unit in title complex

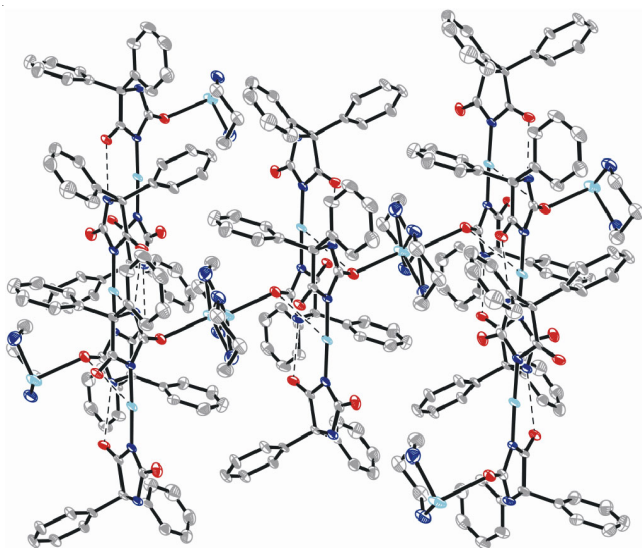


Fig. 2. Packing diagram of the complex

## ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 21101069), Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (13KJB150005), the Open Foundation of Jiangsu Key Laboratory of Marine Biotechnology (No. HS12006) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

## REFERENCES

1. P. Milne, M. Ho and D.F. Weaver, *J. Mol. Struct.*, **492**, 19 (1999).
2. A. Nokhodchi, N. Bolourchian and R. Dinarvand, *Int. J. Pharm.*, **250**, 85 (2003).
3. T. Akitsu and Y. Einaga, *Acta Crystallogr.*, **60**, m524 (2004).
4. T. Akitsu and Y. Einaga, *Acta Crystallogr. C*, **61**, m183 (2005).
5. T. Akitsu, S. Komorita and Y. Kushi, *Inorg. Chim. Acta*, **315**, 18 (2001).
6. T. Akitsu, S. Komorita and H. Tamura, *Inorg. Chim. Acta*, **348**, 25 (2003).
7. T. Akitsu, S. Komorita and A. Urushiyama, *Bull. Chem. Soc. Jpn.*, **74**, 851 (2001).
8. T. Akitsu, S. Komorita, Y. Kushi, C. Li, N. Kanehisa and Y. Kai, *Bull. Chem. Soc. Jpn.*, **70**, 821 (1997).
9. Z. Hu, J. Chen, V. Bayot and A.M. Jonas, *Acta Crystallogr.*, **62**, m1922 (2006).
10. X.L. Hu, X.Y. Xu, T.T. Xu and D.Q. Wang, *Acta Crystallogr.*, **62E**, m2221 (2006).
11. X.L. Hu, X.Y. Xu, T.T. Xu and D.Q. Wang, *Acta Crystallogr.*, **62E**, m2352 (2006).
12. X.L. Hu, X.Y. Xu, T.T. Xu, H.S. Zhang and D.Q. Wang, *Synth. React. Inorg. Met. Org. Nan.-Met. Chem.*, **36**, 701 (2006).
13. X.L. Hu, P.F. Shi, X.Y. Xu, Y. Luan, J.P. Chen and D.Q. Wang, *Acta Chim. Sin.*, **67**, 2517 (2009).
14. X. Hu, P. Shi, X. Xu, F. Yin, Q. Yang and D. Wang, *Acta Chim. Sin.*, **68**, 487 (2010).
15. G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany. (1997).